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PHOTOCHEMISTRY OF ETHYLENE—BIS(TRIPHENYLPHOSPHINE)PLATINUM

S. SOSTERO, O. TRAVERSO *,

Centro di Studio sulla Fotochimica e Reattività degli Stati Eccitati dei Composti di Coordinazione del C.N.R., Istituto di Chimica, Università di Ferrara, Ferrara (Italy)

M. LENARDA,

Facoltà di Chimica Industriale, Università di Venezia, Venezia (Italy)

and M. GRAZIANI

Istituto di Chimica, Università di Trieste, Trieste (Italy)

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Summary

When $[(Ph_3P)_2Pt(C_2H_4)]$ was irradiated in several solvents and at various wavelengths, the results differ with the conditions used. In particular irradiation at 254 nm gives a new alkylplatinum(II) complex by an insertion reaction.

Introduction

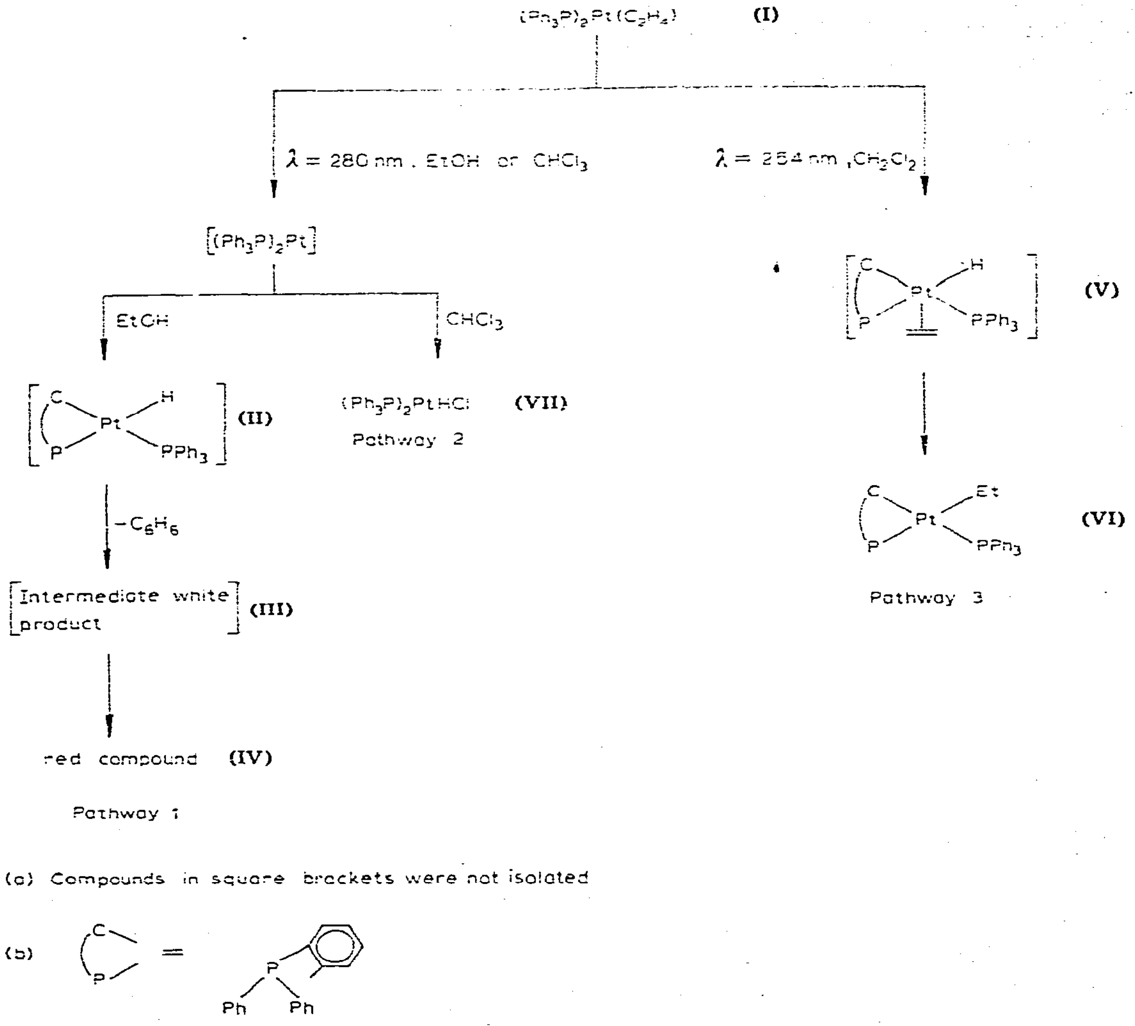
There have been many studies of the photochemistry of square-planar complexes [1]. In the main the photochemical behaviour of these complexes consists largely of photoacceleration of thermal reactions, but photoisomerisation of platinum complexes occurs in some cases [1,2]. This appears to be an intramolecular process occurring by a twisting mechanism, with an excited state having a distorted tetrahedral structure [3]. Little is known, on photochemistry of organometallic complexes of platinum, but we recently reported the photochemical isomerisation of $(Ph_3P)_2Pt[(CN)_2C{=}C(CN)_2]$ to the percyanovinylplatinum(II) complex $(Ph_3P)_2Pt(CN)[C(CN){=}C(CN)_2]$ [4], and of the platinaoxacyclobutane complex: $(Ph_3P)_2\underline{PtOC(CN)_2C}(CN)_2$ to the percyanovinylethanolateplatinum(II) complex $(Ph_3P)_2Pt(CN)[OC(CN){=}C(CN)_2]$ [5]. In both cases migration of cyanide occurs.

To provide a better understanding of the possible steps in these reactions we decided to decrease the number of electron-withdrawing substituents on the unsaturated ligands; we thus studied the photochemical behaviour of $[(Ph_3P)_2Pt$-(fumaronitrile)] [6] and now describe that of $[Ph_3P)_2Pt(C_2H_4)]$.

Results and discussion

[$(Ph_3P)_2Pt(C_2H_4)$] was irradiated in ethanol or a halocarbon at 280 or 254 nm. Depending on the conditions used (wavelength, solvent ect.) different results were obtained as depicted in Scheme 1.

SCHEME 1



(a) Compounds in square brackets were not isolated

(b)

A. *Irradiation at 280 nm*

[$Ph_3P)_2Pt(C_2H_4)$] was irradiated in EtOH at 280 nm, to give a white product which became red on standing or on heating. This analyzes as [$PtP_2Ph_4(C_6H_4)]_2$ and appears to be identical with the product of pyrolysis of $(Ph_3P)_2PtR_2$ [7]. Recently the crystal structure of a compound of very similar composition was reported [8]. The physical data reported for such complexes are, however, insufficient to permit comparison [9]. It should be noted that the formation of dimeric complexes were also reported in the photoreaction of $[(Ph_3P)_2Pt(oxalate)]$ [10,11], in which two different products are obtained.

The first step of the reaction (Scheme 1, Pathways 1 and 2) is probably the photodissociation of C_2H_4 to form $[(Ph_3P)_2Pt]$ (II), as the active intermediate [12,14]. Compound III formed by *o*-metallation was not isolated since it eliminates benzene (detected in the reaction mixture by GLC) to produce IV [7]. The IR spectrum of complex IV shows a sharp band at 730 cm^{-1}, indicative of an *ortho*-metallated phenyl group [15], but $Pt(PPh_3)_n$ complexes also show several bands in this region.

Irradiation in $CHCl_3$ at the same wavelength gives $(Ph_3P)_2PtHCl$, identified by comparison of its ^1H NMR spectrum (τ 26.5t ppm, 1H, J(P—H) 13.5 Hz) and IR spectrum (ν(Pt—H) 2240 cm^{-1}) with those of an authentic sample [16]. It is noteworthy that the NMR spectrum reveals that C_2H_4 is released by the irradiation although does not thermally separate from $[(Ph_3P)_2Pt(C_2H_4)]$ [17]. Thus after 30 min of irradiation at 280 nm the signal of coordinated ethylene τ 7.43 ppm, J(Pt—H) 60 Hz vanished, and a new band due to uncoordinated ethylene (τ 4.65 ppm) appeared; at the same time the hydride signal at τ 26.6 ppm developed.

The formation of $(Ph_3P)_2PtHCl$ could be due to the reaction of an alkoxyplatinum complex (formed by reaction of ROH, which is present as a stabilizing agent [9], with platinum(0) complexes [18,20]), with chlorinated solvent during irradiation.

The ethylene released during the photoreaction was determined by titration [21]. Good linear plots for the released ethylene as function of the irradiation time were obtained. Since the photoreaction is zero-order, the quantum yield for the ethylene photorelease could be calculated (λ 280 nm; ϕ 0.85 in C_2H_5OH; $\phi = 0.83$, in chlorocarbon solvents).

B. Irradiation at 254 nm

Irradiation with light of 254 nm of wavelength gave different results (Pathway 3, Scheme 1). There was no evidence of formation of ethylene or benzene, and the only product isolated was VI, which has been formulated as an alkylplatinum(II) derivative on the basis of elemental analysis and spectroscopic properties. The NMR spectrum shows bands attributable to an ethyl group σ-bonded to platinum (τ 6.77q ppm, τ 8.60t ppm). Bands attributable to phenyl protons are also present, and the integration was as expected for structure VI. However, because of the complexity of the spectrum it was not possible to reach definite conclusions about the arrangement of the ligands. The presence of an intense band in the IR region at 730 cm^{-1}, not present in the parent compound, may be attributable to an *ortho*-metallated phenyl ring [15]. The final product VI [Pathway 3, Scheme 1] was probably formed via a 5-coordinated olefinic hydridoplatinum(II) complex (V) followed by insertion of the ethylene molecule into the Pt—H bond.

Conclusion

The electronic spectra of $[(Ph_3P)_2Pt(C_2H_4)]$ in EtOH and in $CHCl_3$ are shown in Fig. 1. The sharp shoulder at 285 nm can be attributed to a CT band (band A), while the absorption at higher energy (band B) can be assigned to the vibronic

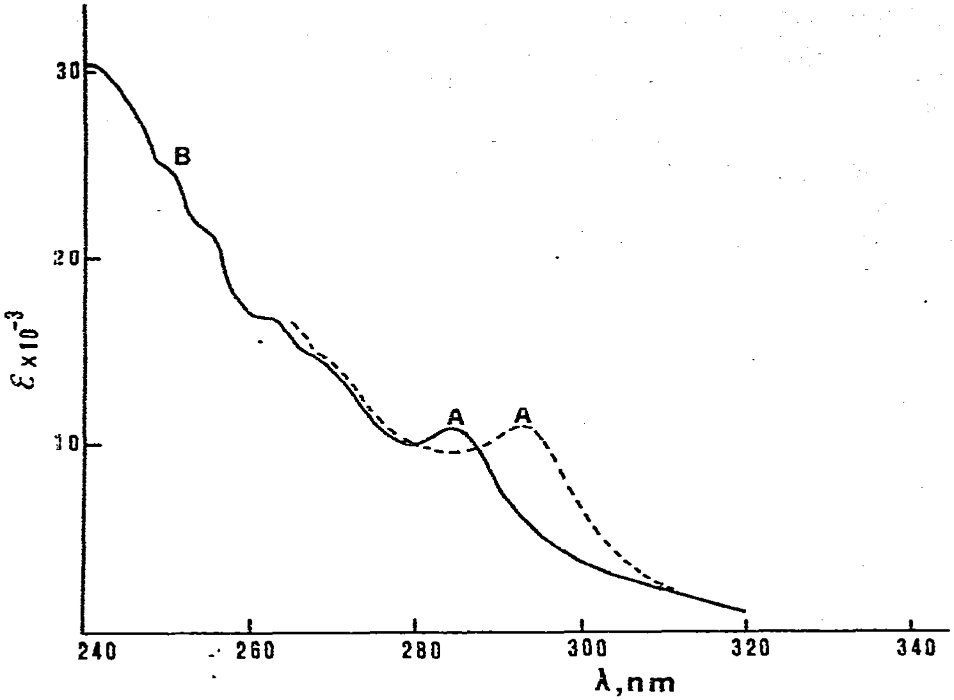


Fig. 1. Electronic spectra of the complex $[(Ph_3P)_2Pt(C_2H_4)]$ in EtOH (———) and in $CHCl_3$ (——).

structure of a π—π* transitions localised on the benzene ring of the PPh_3 ligand [22]. The large solvent effect on the A band in the spectrum of $[(Ph_3P)_2Pt(C_2H_4)]$ has been found to be of the same magnitude (ca. 1.200 cm^{-1} on going from ethanol to chloroform) and in the same direction as those for a number of square-planar platinum complexes [23]. Since the solvent-dependent band in transition metals complexes can be assigned to metal to ligand charge transfer (MLCT) [24], it seems likely that the solvent-dependent A band can be attributed to a MLCT from the platinum orbitals to antibonding orbitals of the ethylene ligand. On the other hand, successive substitution of the H atoms of the coordinated ethylene molecule by cyano groups shifted the A band towards lower energies [25], reflecting the change in the conventional π-back donation in the metal olefin bond.

As a consequence of the electron distribution in the excited state on irradiation at the wavelength of the A band, olefin is released to give $[(PPh_3)_2Pt]$ as active intermediate. The formation of $[(Ph_3P)_2Pt]$ as an intermediate is also supported by the negligible solvent effect on the quantum yield in the photodissociation of ethylene. Pathway 3 (Scheme 1), is followed when the CH_2Cl_2 solution is irradiated at 254 nm, and the final product VI is then formed via a five-coordinate intermediate.

Absorption of $[(PPh_3)_2Pt(C_2H_4)]$ in the region 250—260 nm is attributed to the π—π* transition of the Ph_3P ligand [22]. Since this transition gives an intense band, the absorption due to the Pt—ethylene CT transition is negligible. Irradiation at 254 nm completely suppresses the ethylene dissociation while having a much stronger effect on the phenyl ring of the phosphines. So this type of excitation would be expected to lead to a photoreactive state in which labilization of a hydrogen atom of the phenyl ring occurs, to give compound V, as described in Scheme 1.

Experimental

$[(PPh_3)_2Pt(C_2H_4)]$ was made by a published method [26]. It is thermally stable and it was recovered from alcoholic, chlorocarbon or benzene solutions after refluxing in the dark for several hours. The NMR spectrum of $[(Ph_3P)_2Pt(C_2H_4)]$ in $CDCl_3$ solution shows a broad 1.4.1. triplet at τ 7.59 ppm, due to coordinated ethylene. The signal is not affected by the presence of free olefin, showing ethylene does not appreciably dissociate in solution.

Spectroquality ethanol and chlorocarbon solvents were purchased from Merck. They were used as received, after a check had shown that the same results were obtained using solvents purified by distillation on molecular sieves. $CDCl_3$ was a Merck product and used as received.

Irradiation procedure

Irradiation at 254 nm was carried out with a PGQ immersion mercury lamp, fitted with a UV power supply unit, model Mineral light SCT4. The irradiation vessel was a Pyrex condenser sealed with a greaseless joint. Irradiations were carried out at room temperature. Monochromatic light of 280 nm was obtained from a high pressure Hanau Q400 Mercury lamp and the appropriate Baush and Lomb interference filter.

All the operations were performed under nitrogen, and the solvents were deoxygenated by vacuum freeze-pump-thaw technique. Ethylene analysis was carried out as previously described [21].

Apparatus

The IR spectra were recorded on a Perkin—Elmer 577 instrument and the NMR spectra on a Perkin—Elmer R 24 A instrument. GLC analysis were carried out with a Carlo Erba "Fractovap" instrument.

Synthesis of $[(Ph_3P)Pt(PPh_2C_6H_4)C_2H_5]$ (VI)

A stirred solution of 10^{-2} *M* of $[(Ph_3P)_2Pt(C_2H_4)]$ in 50 ml of CH_2Cl_2 was irradiated at 254 nm using a PGQ mercury lamp for 5 h at room temperature. The mixture was concentrated under reduced pressure, and 40 ml of ethyl ether were added. After removal of some decomposition products by filtration, pentane was added to give a yellow solid, which was crystallized from an ether/benzene mixture. Analysis Found: C, 61.1; H, 4.5; P, 8.3; Pt, 26.1. $PtP_2C_{38}H_{34}$ calcd.: C, 61.05; H, 4.6; P, 8.3; Pt, 26.1%.

Synthesis of $[PtP_2Ph_4C_6H_4]_2$ (IV)

In a quartz reaction vessel a 10^{-2} *M* solution of $[(Ph_3P)_2Pt(C_2H_4)]$ was irradiated under nitrogen at 280 nm. Some decomposition occurred, and a white solid which became red on standing or heating was observed after 20 h. The solid was collected under nitrogen, crystallized from hot benzene, and dried under vacuum. It analysed as $[PtP_2Ph_4C_6H_4]_2$ [7—11]. The evolved gas and the reaction mixture were analyzed by GLC and ethylene and benzene were identified.

Photochemical preparation of $(Ph_3P)_2PtHCl$ (VII)

20 ml of a 10^{-2} *M* solution in $CHCl_3$ of $[(Ph_3P)_2Pt(C_2H_4)]$ were placed in a quartz vessel and irradiated at 280 nm as above. The solvent was removed under reduced pressure to yield a colourless solid, which was identified as $(Ph_3P)_2PtHCl$ by comparison with an authentic sample [16].

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